91. *Physical and Chemical Properties of Organo-metallic Compounds. Part I. The Vapour Pressures and Freezing Points of Simple Metal Alkyls of Groups II, III, and V.*

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Measurements are recorded of the vapour pressures and freezing points of dimethyl-, diethyl-, di-*n*-propyl-, and di-*n*-butyl-zinc, trimethyl-, tri-*n*-propyl-, and tri*iso*propyl-boron, solutions of trimethylboron in *n*-heptane, trimethyl- and triethyl-aluminium, trimethyl- and triethyl-stibine, dimethylcadmium and trimethylbismuth. From the vapour-pressure curves, the boiling points, latent heats of vaporization, and the Trouton constants have been calculated.

THE preparation in a pure state of those metal alkyls which are spontaneously oxidizable at room temperatures presents experimental difficulties which are reflected in the absence, or comparatively wide variations, of recorded values of their physical constants. For example, in the case of the zinc alkyls recorded values of the boiling points differ by 2° for the dimethyl, by 5° for the diethyl and by 14° for the *n*-propyl derivative. No data for the freezing points of boron, aluminium, antimony, cadmium, and bismuth alkyls are available and the vapour-pressure data are scanty or absent.

FIG. 1.

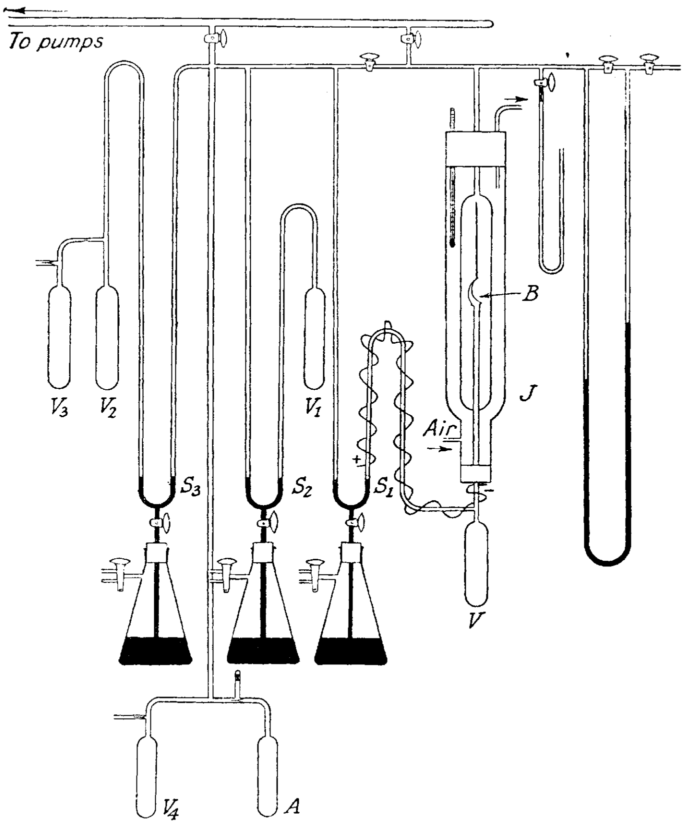
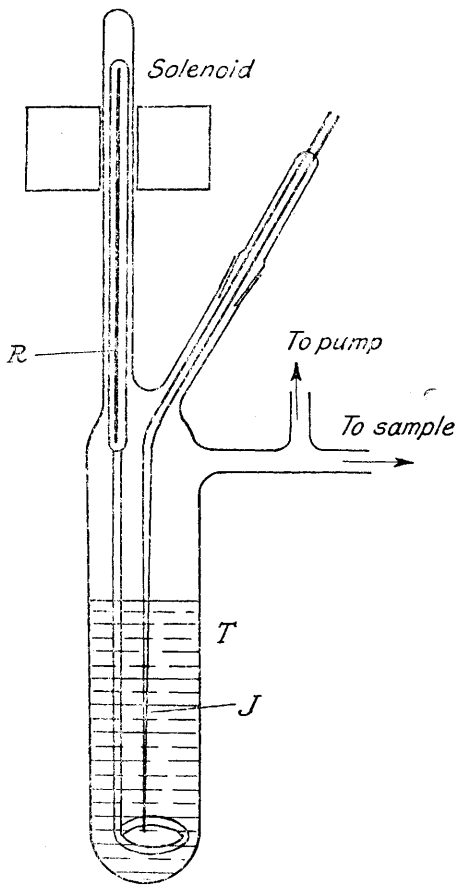


FIG. 2.



In the course of an investigation into the properties of a series of these compounds, described in subsequent papers, advantage has been taken of the availability of pure specimens to determine the vapour pressure–temperature curves, freezing points and, in some instances, the heats of combustion. The vapour-pressure and freezing-point data are included in the present paper.

EXPERIMENTAL.

Determination of Vapour Pressures.—The apparatus employed is shown in Fig. 1. Pressures are measured by a Bourdon gauge *B*, which is maintained at any desired temperature by the air-jacket *J*, and can be read to 0·01 mm.

The tube containing the sample is fitted with a vacuum breaker and is sealed on at A, and the whole evacuated. The breaker is then operated and about one-third of the liquid distilled into V_1, which is then isolated by raising the mercury in the U-tube S_2. The three mercury seals S_1, S_2, and S_3 are employed so that the vapours of the alkyls do not have to pass through taps before their pressures are measured. The middle third is distilled into V_2 and isolated, and the two end fractions united by distilling the liquids in V_1 and in the original container into V_4, which is then sealed off at a constriction. A portion of the middle fraction is taken to V and its vapour pressure determined at a suitable (low) temperature; S_1 is then lowered so that V is connected to the pump for a short time. The vapour pressure is then redetermined, and the process repeated until a consistent value is obtained. The whole vapour-pressure curve is then determined, for both rising and falling temperatures. The heating coil H enables measurements to be made above room temperatures. By adopting this procedure, any thermal decomposition of the alkyl is at once detected. The liquid in V is then pumped away. After distillation of a fraction of the liquid in V_2 to V_3, a further sample is taken to V, and another vapour-pressure curve obtained, to test the homogeneity of the middle fraction in V_2. If satisfactory agreement is obtained, the middle fraction is completely distilled into V_3, which is fitted with a vacuum breaker, and sealed off.

Determination of Freezing Points.—The apparatus employed is shown in Fig. 2. The alkyl is distilled under a vacuum into the tube T, which is then sealed. The cooling curve for the liquid is determined by immersing T in a suitable low-temperature bath and measuring temperatures by a copper–constantan thermocouple J sealed into the vessel. Stirring is effected by means of a totally enclosed magnetic stirrer R.

Results.—The vapour-pressure data are shown in Figs. 3 and 4 as plots of $\log_{10}p$ and the reciprocal of the absolute temperature. In general, the relationship is linear over the indicated temperature range, and the data may conveniently be summarised in the form of an equation $\log_{10}p = -A/T + B$. The boiling points (extrapolated) and latent heats of vaporization (L) are derived from the vapour-pressure data.

In most instances the alkyls gave sharply defined freezing points which could be estimated with an accuracy of $\pm 0{\cdot}15°$. An exception was di-*n*-propylzinc, which became very viscous in the neighbourhood of its freezing point and eventually solidified to a transparent glass. After standing for several hours the solid tended to crystallize.

The values of A and B in the above equation and the other physical constants are given in the accompanying table, L/T being Trouton's constant.

The Zinc Alkyls.—The data for the four zinc alkyls are shown in Fig. 3.

	Values in v.-p. formula.					
Alkyl.	A.	B.	B. p./ 760 mm.	L, cals./mol.	L/T.	F. p.
$ZnMe_2$ [1]	1560	7·802	44°	7,150	22·5	− 29·2°
$ZnEt_2$ [2]	2109	8·280	117·6	9,605	24·6	− 30·0
$ZnPr^{\alpha}_2$	2099	7·969	139·4	9,620	23·3	−81 to −84
$ZnBu^{\alpha}_2$	2241	7·608	201·1	10,260	21·7	− 57·7
BMe_3 [3]	1250 *	7·906 *	−21·8	5,721	22·8	−153
BPr^{α}_3	2085	7·662	164·5	9,550	21·8	− 65·5
BPr^{β}_3	2091	7·862	147·4	9,570	22·8	− 52·5
$AlMe_3$ [4]	2148 †	8·279 †	125·3	9,830	24·7	15·0
$AlEt_3$ [5]	2826	8·778	207·0	12,930	26·9	—
$SbMe_3$	1627	7·496	80·6	7,450	21·1	− 62·0
$SbEt_3$	2183	7·904	161·4	9,993	23·0	− 98·0
$CdMe_2$	1850	7·764	105·7	8,468	22·3	− 4·2
$BiMe_3$	1815	7·659	107·1	8,308	21·8	− 85·8

* Up to 450 mm. † Over the temperature range 17—100°.

[1] I.C.T. give b. p. 45—47°, f. p. −40°. Thompson and Linnett (*Trans. Faraday Soc.*, 1936, **36**, 681) give b. p. 46·9°, L 6840.

[2] I.C.T. give b. p. 118°, f. p. −28°, −22°. Thompson and Linnett (*loc. cit.*) give b. p. 123°, L 8780.

[3] Stock and Zeidler (*loc. cit.*) give b. p. −20·2°/760 mm.

[4] Laubengayer and Gilliam (*loc. cit.*) give $A = 2104$, $B = 8{\cdot}125$ (temp. range, −23° to −70°); b. p. 126·1°; L 9600; L/T 24·1.

[5] Laubengayer and Gilliam (*loc. cit.*) give $A = 3625$, $B = 10{\cdot}784$ (temp. range, 110—140°); b. p. 185·6°; L 16,660; L/T 36·2.

Dimethylzinc. Vapour pressures were determined over the temperature range −25° to +45°, corresponding to a pressure range 30—770 mm. of mercury. The $\log_{10}p$–$1/T$ plot is linear over practically the whole range, with a slight but perceptible falling off in the region of highest pressure. The data were readily reproducible in different determinations, and also for rising and falling temperatures.

*Di-*n*-propylzinc.* Above about 70° thermal decomposition of the alkyl becomes perceptible, and at 100° it can be followed on the Bourdon gauge.

*Di-*n*-butylzinc.* Vapour pressures were determined up to 120° (75 mm.), no decomposition being detectable even at the highest temperature.

Boron Alkyls.—The vapour-pressure data for three alkyls are shown in Fig. 4.

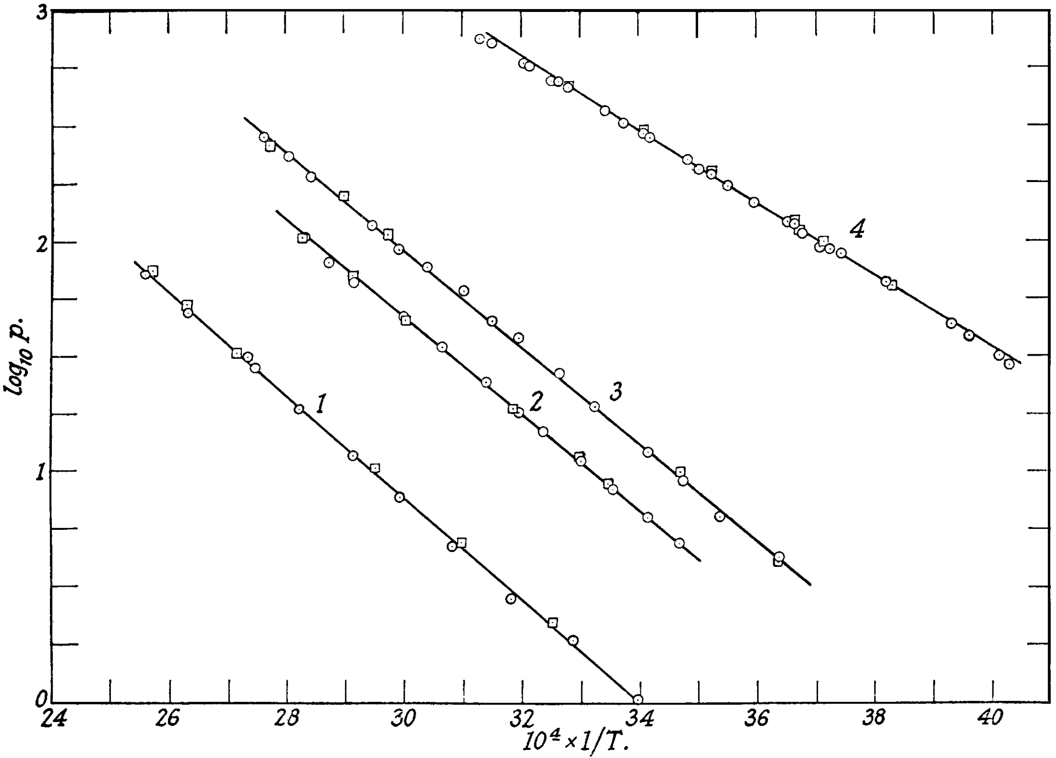
Trimethylboron. Six separate determinations of the vapour-pressure curve were made, but although agreement between them was fairly good, it was less so than with the other alkyls studied. Variations were almost certainly due to small traces of dissolved gas remaining in the liquid at the low temperatures used (−90° to −20°). The $\log_{10}p$–$1/T$ plot is linear only up to about 450 mm., above which the measured pressures are lower than would correspond with a linear relationship. The data of Stock and Zeidler (*Ber.*, 1921, **54**, 531) agree with the present results up to about 350 mm. but deviate more from linearity at higher pressures.

*Tri-*n*-propylboron.* Vapour pressures were determined over the range 0—120°, the highest pressures being about 200 mm. Pressure values determined during cooling were always slightly higher than those obtained with rising temperatures, possibly owing to traces of dissolved gas.

*Triiso*propylboron.* After careful fractionation in a vacuum to remove ether and dissolved gases, the compound gave reproducible vapour pressures inthe range 0—120°, there being no indication of thermal decomposition.

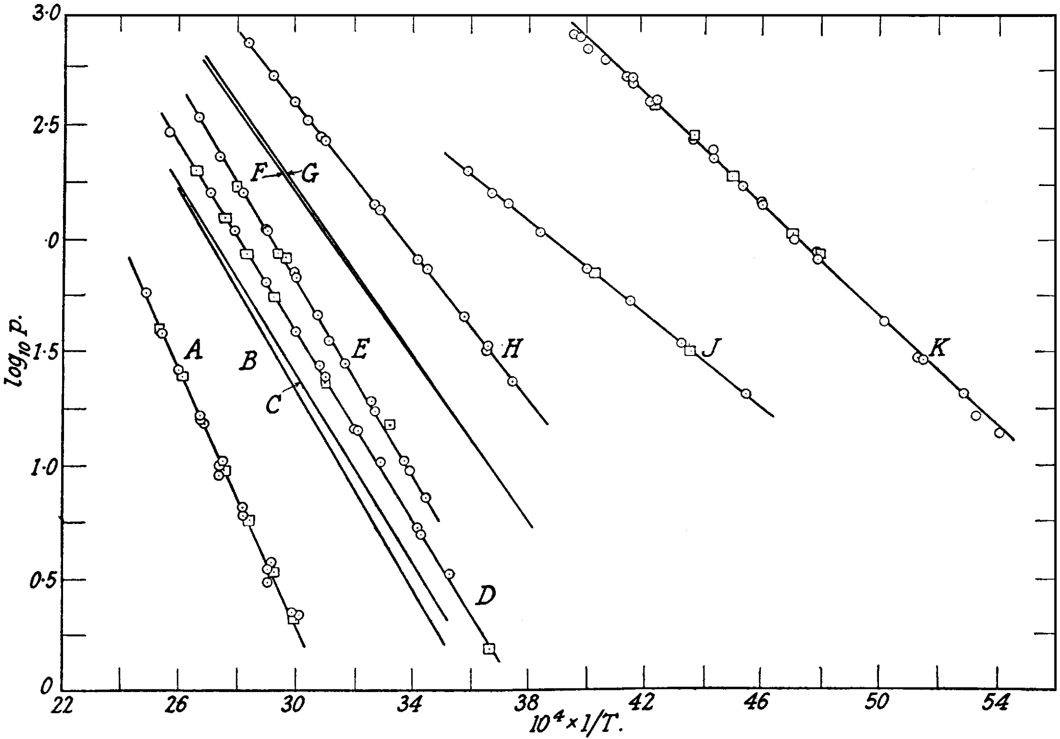
Solutions of trimethylboron in n-*heptane.* The experimental procedure was to condense separately measured quantities of the solvent and the alkyl vapours, warm them slowly to 0° and allow them to mix. The approach to equilibrium, which required several hours for completion, was accompanied by a steady decrease in pressure. Measurements of

FIG. 3.



1. *Di-*n-*butylzinc.* 2. *Di-*n-*propylzinc.* 3. *Diethylzinc.* 4. *Dimethylzinc.*

FIG. 4.



A. *Triethylaluminium.* B. *Triethylstibine.* C. *Tri-*n-*propylboron.* D. *Triisopropylboron.*
E. *Trimethylaluminium.* F. *Dimethylcadmium.* G. *Trimethylbismuth.* H. *Trimethylstibine.*
J. 5·64% *soln.* $B(CH_3)_3$ *in* n-*heptane.* K. *Trimethylboron.*

the vapour pressure were made with falling and with rising temperatures, corrections being applied for the changes in composition of the two phases with temperature. The following solutions were used :

(1) 5·64 G. of BMe_3 per 100 g. of solution (Mol.-fractn. of BMe_3 = 0·096)
(2) 10·43 G. ,, ,, ,, (,, ,, ,, = 0·180)
(3) 14·33 G. ,, ,, ,, (,, ,, ,, = 0·230)

The log $_{10}p$–$1/T$plots for the three solutions are given in Fig. 4. The vapour pressures are about 20% higher than would be predicted from Raoult's law and, in consequence, the latent heats are lower than that of the pure alkyl.

The data are summarised below :

% Alkyl in solution.	Vapour pressure.	Partial pressure at 20°, mm.	L, cals./mol.
5·64	$\log_{10} p = -1033/T + 5{\cdot}996$	302	4730
10·43	$\log_{10} p = -1004/T + 6{\cdot}214$	603	4593
14·33	$\log_{10} p = -1093/T + 6{\cdot}592$	832	5005

The Aluminium Alkyls.—The vapour-pressure data are shown in Fig. 4.

Trimethylaluminium. Vapour pressures were measured up to 100° without any sign of decomposition, the results being satisfactorily reproducible. This substance is, however, associated in the vapour state and there is a progressive decrease in its apparent molecular weight over the temperature range employed. Laubengayer and Gilliam (*J. Amer. Chem. Soc.*, 1941, **63**, 477) have shown that the molecular weight in the neighbourhood of 70° corresponds to that of the dimer.

The difference in the two vapour-pressure equations is in large part attributable to the different ranges of temperature employed and the occurrence of dissociation.

Triethylaluminium. This compound has a low volatility and distils extremely slowly in a vacuum. It was, therefore, necessary to make the pressure measurements directly with a mercury manometer. After prolonged pumping to remove dissolved gases, measurements were made in the range 40—125° (pressures up to 58 mm.).

According to Laubengayer and Gilliam triethyaluminium is about 12% associated to the dimer at 150·6°; they also note that, when heated above 165°, it undergoes a decomposition which involves a decrease of the number of molecules in the vapour state. They point out that their value for the heat of vaporization is probably too high because it includes some heat of dissociation.

The Antimony Alkyls.—Trimethylstibine. The pure liquid gave closely reproducible pressures on heating and cooling.

Triethylstibine. Pressures were measured over the range 0—120° without any evidence of decomposition.

The determination of the data for the cadmium and the bismuth alkyls does not require any special comment.

Preparation and Purification of Alkyls.—Dimethylzinc. The method described by Greenlaw and Renshaw (*J. Amer. Chem. Soc.*, 1920, **42**, 1472), in which the appropriate alkyl iodide is heated with a zinc–copper couple, was employed. 36 G. of methyl iodide, with 110 g. of the couple and 2 drops of ethyl acetate, afforded a 90% yield of crude substance.

Diethylzinc. By the above procedure 65 g. of ethyl iodide and 165 g. of zinc–copper couple gave a 95% yield of crude diethylzinc.

*Di-*n*-propylzinc.* The method described by Noller (*J. Amer. Chem. Soc.*, 1929, **51**, 594), in which a couple containing 5—8% of copper is heated with equimolecular quantities of alkyl iodide and bromide, was employed, 85 g. of the iodide and 61·5 g. of the bromide (with 130 g. of the couple) giving an 85% crude yield.

*Di-*n*-butylzinc.* This was prepared from *n*-butyl iodide by the above method.

Purification of the zinc alkyls. The crude product contains alkyl iodide (and bromide), which can best be removed by two or three passages over a zinc–copper couple heated electrically to about 150°. Any hydrocarbon impurity arising from the decomposition of the alkyl can be removed by distillation under reduced pressure. The absence of alkyl iodide in the purified product was confirmed by the absorption spectrum.

*Trimethyl-, triethyl-, tri-*n*-propyl-, and tri*iso*propyl-boron.* By passing dry boron trifluoride into the appropriate Grignard reagent yields representing about 50% of the theoretical were obtained.

Trimethylaluminium. By heating dimethylmercury (124 g.) with excess of aluminium powder (15 g.) in a sealed tube at 100° for 24 hours and fractionating the product in a vacuum, a nearly theoretical yield was obtained.

Triethylaluminium. Similarly, diethylmercury (20 g.) and aluminium (6 g.) gave an almost theoretical yield.

Trimethylstibine. This was prepared by the action of antimony trichloride on the Grignard reagent. A satisfactory separation of the alkyl from ether could not be obtained by fractionation in a vacuum, so the product was isolated *via* the dibromide, $SbMe_3Br_2$. This was prepared by running bromine into the ethereal solution of trimethylstibine until the liquid was just coloured. The dibromide was filtered off, washed with alcohol and ether, and dried (yield *ca.* 65%); it was decomposed by heating to 150° under reduced pressure with an excess of finely granulated zinc and a few c.c. of water. The product, consisting of trimethylstibine and a little water, was dried over calcium chloride and purified by fractionation in a vacuum. Materials : methyl iodide, 142 g. ; magnesium, 24 g. ; absolute ether, 800 c.c. ; antimony trichloride, 74 g. in 300 c.c. of ether. Yield, 45%.

Triethylstibine. This was prepared by the action of antimony trichloride (74 g. in 300 c.c. of ether) on the Grignard reagent (Mg, 24 g. ; EtI, 156 g. ; ether, 800 c.c.). The bulk of the ether was distilled off under reduced pressure, and pure triethylstibine obtained by fractionation of the product in a vacuum. Purification by means of the dibromide was not necessary. Yield 60%.

Dimethylcadmium. This was similarly prepared ($CdBr_2$, 100 g. in 200 c.c. of ether; MeI, 142 g. ; Mg, 24 g. ; ether, 400 c.c.). The ether was separated by repeated fractionation under reduced pressure and in a vacuum. Yield 80%.

Trimethylbismuth. By the same procedure as in the preceding case ($BiCl_3$, 76 g. in 300 c.c. of ether; MeI, 107 g. ; Mg, 18 g. ; ether, 500 c.c.), a 40% yield was obtained.

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